Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

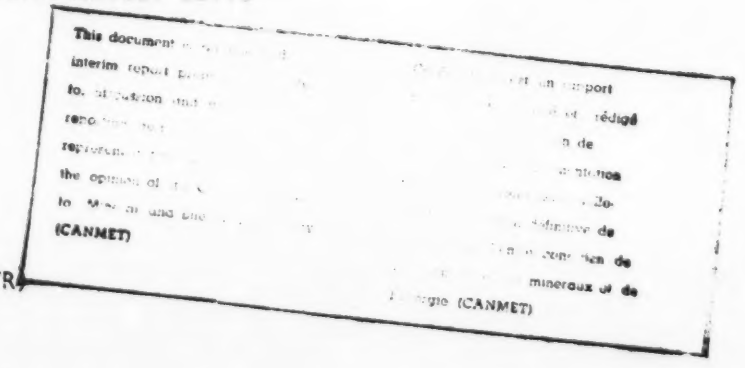
CANADIAN CONTRIBUTION TO IEA PROGRAMME OF RESEARCH AND DEVELOPMENT ON THE PRODUCTION OF HYDROGEN FROM WATER; TASK VI, PHOTOCATALYTIC WATER ELECTROLYSIS - 1984 (SUMMARY OF WORK IN PROGRESS)

S.M. Ahmed
Physical Chemistry Section
Extractive Metallurgy Laboratory

December 1984

For submission to the IEA, Task VI, Programme

Project: ERP-4.5.5.0.02
Materials for Photoelectrochemical Cells



6 AP

ENERGY RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT ERP/MSL 84-165 (TR

FEB 27 1985

MICROMEDIA

CANADIAN CONTRIBUTION TO IEA PROGRAMME OF RESEARCH AND DEVELOPMENT ON THE PRODUCTION OF HYDROGEN FROM WATER; TASK VI, PHOTOCATALYTIC WATER ELECTROLYSIS - 1984 (SUMMARY OF WORK IN PROGRESS)

by

S.M. Ahmed*

RACT

The task VI of the International Energy Agency, is devoted to a program of research and development on the "Photocatalytic Water Electrolysis" on semiconductor surfaces for the production of hydrogen using sunlight. CANMET's contribution to this programe amounts to one person year in this field. This report is a summary of the work in progress at CANMET during the year 1984, to be submitted to IEA, Task VI.

* Research Scientist, Physical Chemistry Section, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1.

CONTRIBUTION CANADIENNE AU PROGRAMME DE L'AIE DE RECHERCHE ET DE DÉVELOPEMENT SUR LA PRODUCTION D'HYDROGÈNE DE L'EAU; TÂCHE VI, ELECTROLYSE PHOTOCATALYTIQUE DE L'EAU, 1984 (PRÉCIS DES TRAVAUX EN COURS)

par

S.M. Ahmed

RÉSUMÉ

L'Agence internationale de l'énergie, dans le contexte de la Tâche VI, s'est consacree à un programme de recherche et de développement de l' "Electrolyse photocatalytique de l'eau sur les surfaces des semiconducteurs pour la production d'hydrogène avec de la lumière solaire. La contribution de CANMET à ce programme est l'équivalent d'un homme-année dans ce domaine. Ce rapport est un résumé du travail en cours à CANMET durant 1984. Il sera soumi à l'A.i.e. (tâche VI).

CANADIAN CONTRIBUTION TO IEA PROGRAMME OF RESEARCH AND DEVELOPMENT ON THE PRODUCTION OF HYDROGEN FROM WATER

TASK VI, PHOTOCATALYTIC WATER ELECTROLYSIS - 1984

Project Leader: S.M. Ahmed, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources Canada, Ottawa, Canada

Consultant: Professor S.R. Morrison, Director, Energy Research Institute, Simon Fraser University, Burnaby, British Columbia, Canada

Summary of Work in Progress

1. Extended Studies on Screen Printed TiO_2 Films

During the course of investigations of TiO_2 films it was found that although the rutile form of TiO_2 can be reduced readily at temperatures as low as 550°C, the anatase form requires higher temperature for reduction. The reduction rate is slow at 800°C, becomes appreciable at 850°C and fast at 900°C. Furthermore, X-ray investigations have revealed that the anatase form is immediately converted into the rutile form, on reduction with hydrogen. In one experiment, a 3/4 h reduction of anatase at 850°C, with 25% H_2 in flowing Ar, resulted in a mixture of anatase and rutile with partial reduction, while at 900°C, conversion to rutile was 100% and the material was also heavily reduced. Such reduction, or transformation of anatase to rutile does not occur below 800°C. However, it is well known that certain impurities (e.g., Cu) can also accelerate the anatase to rutile transformation. The significance of this finding in preparing the so-called anatase form of TiO_2 powders in semiconductor form is worth considering, for a reduced form of anatase does not seem to exist. It appears that the Ti^{3+} and Ti-OH species that are formed in the TiO_2 lattice, on hydrogen reduction, lead to the structural change. This phenomenon is still under investigation and the work so far is still semiquantitative.

In further PEC studies of the screen-printed TiO_2 films, doped with Al_2O_3(Ti:Al = 20:1), a previous report has been confirmed that H_2O_2 is the major oxidation product on the photoanode. Unless this product is physically prevented from migrating to the cathode, particularly on TiO_2 particle

suspensions, its cathodic reduction would supercede all other processes, particularly hydrogen evolution if any. Such back reactions could possibly be prevented in the TiO_2 suspensions, by chemical reduction of H_2O_2 with other reagents such as $SO_3^{=}$.

It is obvious from the above reasoning that all efficiency measurements in photoelectrolysis, particularly under short circuit conditions, should be carried out in a two-chamber cell with a diaphragm. It was also found essential that the platinum counter electrode by electrolytically reduced before efficiency measurements to remove any oxide film, and that the electrolyte solution be purified by a pre-electrolysis run for several hours to remove metal impurities. Failing these precautions, spurious results are obtained in efficiency measurements in photoelectrolysis.

2. Surface Modifications of GaAs

The effects of electrochemically deposited cobalt films of 10 nm, 20 nm and 50 nm thickness, on n- and p-GaAs, were investigated by studying the PEC response and by impedance measurements. Without annealing, the cobalt deposited GaAs gave large dark currents and very poor photocurrents. However, the Mott-Schottky plot for such electrodes was linear even at potentials close up to the fbp, most probably due to the elimination of the surface states by cobalt. After sintering at 250°C in an inert atmosphere, the photocurrents at low band bending were reduced while the photocurrents at large band bending recovered to the original value when the cobalt film was only 10 nm. With thicker Co films, GaAs gave much lower photocurrents throughout, even after sintering. It appears that cobalt after diffusion into the GaAs surface provides centres for electron-hole recombination, particularly at low band bending. The charge separation is still efficient with 10 nm Co films at large band bending. Thicker Co films could also reduce light penetration.

Photocorrosion of GaAs with Co films was tested during prolonged experiments, lasting several hours, followed by SEM and microprobe analysis of the surface. The resultant surface consisted of highly corroded areas and totally non-corroded areas. The non-corroded areas showed cobalt concentration on the surface, as indicated by the microprobe analysis. Thus cobalt films does seem to prevent photocorrosion of GaAs while the photocorrosion would still proceed through pin holes which are hard to prevent in a thinly deposited film. Cobalt films deposited on p-GaAs result in large dark currents.

A large increase in photocurrents was experienced after electrodepositing thin platinum films on n-GaAs, as a result of improvements in charge transfer kinetics. However, the problem of photocorrosion of GaAs photoanodes is still predominant. The work still continues to improve the collection efficiency and charge transfer kinetics and prevent photocorrosion of GaAs and Si by surface modifications.

3. Other Activities

Construction of equipment for luminescence spectroscopy at the semiconductor-solution interface using a He-Cd laser at 325 nm and 442 nm and a He-Ne laser at 632 nm, is near completion and relevent investigation work will soon be started. Other equipment now available includes a computer controlled LCR meter (Hewlett Packard) for impedance analysis and a magnetron sputtering unit for d.c. and r.f. sputtering.

Outside contract work is being negotiated to develop processes, at a laboratory scale, for the removal of H_2S (H_2 by-product) from natural gas and of CN^-, $S_2O_3^{2-}$ and SO_3^{2-} pollutants from metallurgical effluents from oxidation using semiconductor powder suspensions. In-house work is also starting soon in this field.

Semiconductor catalysts are also being investigated for organic reactions with the ultimate objective of producing liquid hydrocarbons starting from CH_4 in natural gas and from bio-mass products. This work has been contracted to Professor Morrison's group at Simon Fraser University and is being reported separately.

Other Participating Scientists: J. Leduc and J. Trudel

Publications and Reports

1) S.M Ahmed; "The Canadian Contribution to the I.E.A. Work on Hydrogen Production by Photoelectrolysis of Water" Proc. Vth World Hydrogen Energy Conference, Toronto, 1984, eds. T.N. Veziroglu and J.B. Taylor, Pub. Internl. Assocn. for Hydrogen Energy, Vol. 3, pp. 1013-1026.

2) S.M. Ahmed, Aftab Ahmad, S.F. Haller, C. Blaauw and H.M. Naguib; "Photoelectrochemical Studies of the Screen Printed TiO_2 Films" Electrochem Soc., October 7-12, 1984, New Orleans Meeting, Extended Abs. #563, p. 822-823. Full paper in preparation.

3) J. Leduc and S.M. Ahmed; "Impedance Measurements of the Semiconductor-Solution Interface", CANMET Report 84-14E (in editorial processing), Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, 555 Booth Street, Ottawa, Canada.